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GROWTH OF SAPPHIRE FILAMENTS

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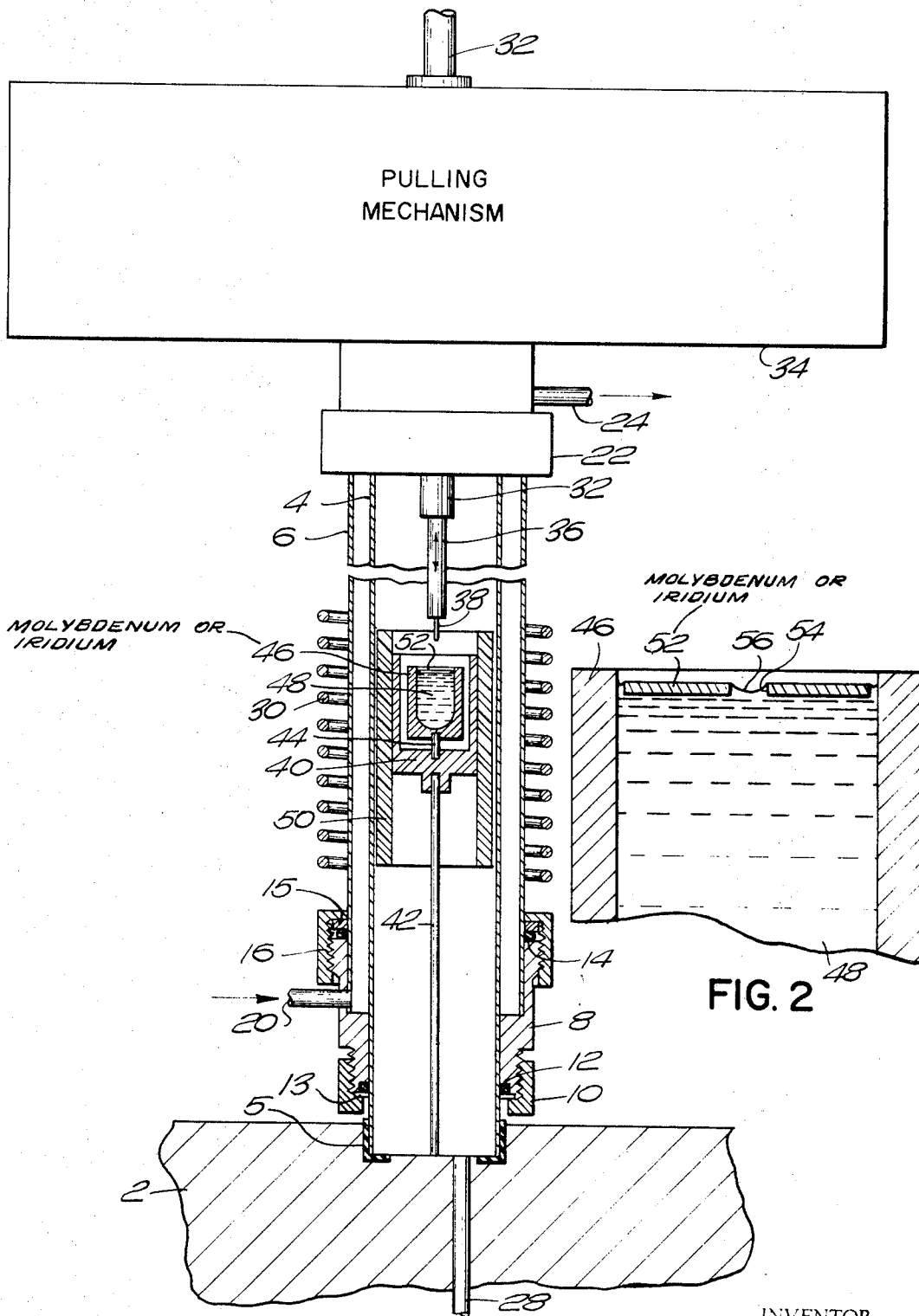


FIG. 1

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GROWTH OF SAPPHIRE FILAMENTS

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12 Claims

ABSTRACT OF THE DISCLOSURE

Method and apparatus for growing elongate filaments of alpha-alumina from an alumina melt contained in a crucible. The invention comprises use of a floating plate to help establish the necessary thermal distribution in the melt, with the plate having an aperture through which a seed is introduced to the melt and the filament is pulled. The plate is made of a material that reduces radiative heat loss from the melt surface.

This invention relates to production of filaments of refractory materials and more particularly to filaments of α -alumina.

This invention is related to the inventions disclosed and claimed in the following co-pending applications of Abraham I. Mlavsky and Harold E. La Belle, Jr.: Ser. No. 621,731, filed Feb. 14, 1967, now abandoned, for "Method And Apparatus For Growing Inorganic Filaments"; and Ser. No. 666,304, filed Sept. 8, 1967, for "Method And Apparatus For Growing Inorganic Filaments, Ribbon From The Melt."

It is recognized that certain refractory materials exhibit improved mechanical properties when produced in fiber or filament form and that composite materials consisting of solid matrices reinforced by such fibers have enormous potential usefulness in the fabrication of strong heat resistant components for turbines, jet engines, missiles, rockets and other high performance equipment. A number of different refractory materials have been suggested for use as a reinforcing or strengthening elements, including boron, borides, carbides, nitrides and oxides, such as SiC, Zr_2O_3 , B_4C , MgO, BeO and Al_2O_3 .

α -Alumina is of particular interest because of its high melting point, high modulus of elasticity and tensile strength. However, while various methods have been developed for growing single crystal fibers of α -alumina, the fibers are almost always of short length and small diameter, typically no longer than 6–7 mm. long and 0.01 mm. thickness. Attempts to produce longer fibers have been fruitless or only partially successful and it has not been possible to grow extended filaments. While small single crystal fibers (also called "whiskers") exhibit very large tensile strengths and, therefore, have utility as reinforcing elements in composite materials, they are difficult to handle.

Accordingly it is an object of this invention to provide α -alumina in extended filament form.

Another object of this invention is to grow α -alumina filaments from the melt. Growth of crystalline material from an open melt customarily occurs in one of two different ways. In one case growth occurs above the surface of the melt, typically according to the Czochralski technique. In the other case growth occurs below the surface of the melt. The latter method is known as dendritic growth and occurs only in a supercooled melt. As a seed grows down into the body of the melt, it is withdrawn at a rate sufficient to keep the growth section below the melt surface. Typical of the successful prior art processes involving dendritic growth from the melt are those developed for growing silicon and germanium.

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Each of these materials is characterized by a discrete twin morphology so that dendritic growth is easily possible. So-called "web" silicon used in semiconductor applications is sheet silicon pulled from the melt as the connecting member between two parallel dendrites. Relatively few other crystalline materials have been grown dendritically from the melt in extended ribbon or filament form.

Accordingly it is a further object of this invention to apply the concept of dendritic growth to produce α -alumina in extended filament form from the melt.

A more specific object is to provide a method and apparatus adapted to produce α -alumina in filaments of extended length by continuous dendritic growth from the melt.

A further specific object is to produce sapphire and ruby filaments by continuous dendritic growth from the melt. Sapphire is pure α -alumina in single crystal form whereas ruby is α -alumina with some of the aluminum atoms in its crystal lattice replaced by chromium.

The foregoing and other objects are attained by providing a melt of α -alumina, establishing a thermal distribution within the melt conducive to dendritic propagation vertically in the melt, introducing a seed into a supercooled region of the melt for a period sufficient for dendritic growth to be initiated, and then withdrawing the seed at a rate approximately equal to the rate at which α -alumina dendrite grows downward into the melt. Proper thermal distribution within the melt is achieved by novel means located on top of the melt but designed so as not to interfere with withdrawal of the seed and the α -alumina filament grown thereon.

Objects and many of the attendant advantages of my invention are believed to be apparent from the following detailed description which is to be considered together with the accompanying drawings, wherein:

FIG. 1 is an elevational sectional view, partly in schematic form, of a preferred apparatus for carrying out the process of this invention; and

FIG. 2 is a magnified sectional view of part of the apparatus of FIG. 1.

Experiments have demonstrated that from an open melt, α -alumina tends to grow circumferentially, i.e., radially from the seed, rather than propagate down into the melt. Dendritic growth when it occurs is parallel to the surface of the melt and often is characterized by branching of the dendrites. Variations in pulling speed do not change the direction of dendritic propagation. Further experiments have indicated that the thermal distribution within the melt is an extremely important parameter affecting continuous dendrite propagation in a vertical direction.

I have discovered that α -alumina dendrites can be made to propagate vertically into the melt and that α -alumina can be pulled from the melt as a continuous filament by providing a plate of selected material that floats on the surface of the melt and has an orifice through which the grown crystal can be pulled. This orifice plate does not function as a die, i.e., the melt is not "extruded" through its orifice; instead the floating orifice plate appears to function as a heat shield in that it modifies the thermal distribution within the melt in a manner conducive to vertical rather than horizontal propagation of dendrites.

Referring now to FIG. 1, the illustrated apparatus provided in accordance with the present invention comprises a vertically moveable horizontal bed 2 on which is supported a furnace enclosure consisting of two concentric-spaced quartz tubes 4 and 6. At its bottom end the inner tube 4 is positioned in an L-gasket 5 in the bed. Surrounding tube 4 is a sleeve 8 that screws into

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collar 10. Between sleeve 8 and collar 10 is an O-ring 12 and a spacer 13. The O-ring 12 is compressed against tube 4 to form a seal. The upper end of sleeve 8 is spaced from tube 4 so as to accommodate the bottom end of tube 6. The bottom end of tube 6 is secured in place by an O-ring 14 and a spacer 15 compressed between a collar 16 that screws onto sleeve 8. Sleeve 8 is provided with an inlet port fitted with a flexible pipe 20. The upper ends of tubes 4 and 6 are secured in a head 22 so that they remain stationary when the bed is lowered. Head 22 has an outlet port with a flexible pipe 24. Although not shown, it is to be understood that head 22 includes means similar to sleeve 8, O-rings 12 and 14, and collars 10 and 16 for holding the two tubes in concentric sealed relation. Pipes 20 and 24 are connected to a pump (not shown) that continuously circulates cooling water through the space between the two quartz tubes. The interior of the furnace enclosure is connected by a pipe 28 to a vacuum pump or to a regulated source of inert gas such as argon or helium. The furnace enclosure also is surrounded by an R.F. heating coil 30 that is coupled to a controllable 500 kc. power supply (not shown) of conventional construction. The heating coil may be moved up or down along the length of the furnace enclosure and means (not shown) are provided for supporting the coil in any selected elevation. At this point it is to be noted that the circulating water not only keeps the inner quartz tube at a safe temperature but also absorbs most of the infrared energy and thereby makes visual observation of crystal growth more comfortable to the observer.

The head 22 is adapted to provide entry into the furnace enclosure of an elongate pulling rod 32 that is connected to and forms part of a conventional crystal pulling mechanism represented schematically at 34. Although not described in detail it is to be understood that the pulling mechanism 34 is adapted to move pulling rod 32 axially and also to rotate it on its axis, both at controlled rates. Pulling rod 32 is disposed coaxially with the quartz tubes 4 and 6 and its lower end has an extension in the form of a metal rod 36 that is adapted to function as a holder for a seed crystal 38.

Located within the furnace enclosure is a cylindrical heat susceptor 40 made of carbon. The top end of susceptor 40 is open but its bottom end is closed off by an end wall. The susceptor is supported on a tungsten rod 42 that is mounted in bed 2. Supported within susceptor 40 on a short tungsten rod 44 is a crucible 46 adapted to contain a suitable supply of alumina 48. The crucible is made of a material that will withstand the operating temperatures and will not react with or dissolve in the molten alumina. In the illustrated embodiment the crucible is made of molybdenum, but it also may be made of iridium or some other material with similar properties with respect to molten alumina. The molybdenum crucible must be spaced from the susceptor since there is a eutectic reaction between carbon and molybdenum at about 2200° C. The inside of the crucible is of constant diameter and may have a hemispherical bottom. In order to obtain the high operating temperatures necessary for the process, a cylindrical radiation shield 50 made of carbon cloth is wrapped around the carbon susceptor. The carbon cloth does not appear to couple directly to the R.F. field but greatly reduces the heat loss from the carbon susceptor. At a given R.F. power setting the shield 50 increases the susceptor temperature by as much as 500° C.

In addition to the supply of alumina, the crucible contains a heat shield in the form of an orifice plate 52 that is made of molybdenum and floats on the surface of the melt. The orifice plate is made with smooth polished surfaces and preferably has a thickness in the range of 0.25 to 1 mm. The plate is shaped to conform to the interior of the crucible and as shown in FIG. 2 is sized so as to provide clearance sufficient for it to float evenly on the melt and to move down in the crucible as the melt is depleted. A clearance of about 0.010 inch suffices. As illus-

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trated in FIG. 2, the orifice plate has a centrally located circular orifice 54. Preferably the orifice has a diameter of about $\frac{1}{16}$ inch, but equally satisfactory results have been obtained with orifices measuring $\frac{1}{32}$ inch. An orifice larger than $\frac{1}{16}$ inch also may be used provided its cross-sectional area is not so large with respect to the overall size of the plate to prevent the latter from establishing the proper thermal distribution in the melt.

The effect of the orifice plate on the growth process is confirmed by experiments to propagate Al_2O_3 filaments continuously using the apparatus of FIG. 1 in the manner described below but with the plate omitted from the crucible. In these experiments a mass of alumina was melted, slowly cooled until solidification proceeded (this is to establish the melting point), remelted, and slowly cooled again to within a few degrees above the melting point. A seed with its C-axis parallel to the axis of the crystal holder was then inserted into the melt and rapidly withdrawn at a predetermined rate. These experiments succeeded in propagating dendrites parallel to the surface of the melt but failed to grow any dendrites down into the melt. This propagation behavior suggested an improper thermal distribution within the melt. Accordingly additional experiments were conducted using the same procedure but supplying more heat to the bottom of the crucible (relative to its sides). This was achieved by shifting the relative positions of the susceptor and the R.F. coil. These additional experiments succeeded in dendritic growth clearly propagated vertically into the melt, but the propagation was not continuous. Dendrites grown in this manner always grew downward from a much larger mass of solidified $\alpha\text{-Al}_2\text{O}_3$, and would stop growing vertically as the larger mass was withdrawn. This behavior suggested that although the increased heat applied to the bottom of the crucible appeared to improve the thermal distribution within the melt enough to promote vertical dendritic growth, removal of the larger mass of solidified α -alumina from the melt caused a thermal fluctuation sufficiently larger to prevent further vertical propagation.

Introduction of the orifice plate onto the surface of the melt solved the problem of continuous growth of α -alumina and confirmed that in order to obtain continuous dendritic propagation vertically into the melt, it is necessary not only to establish a critical thermal distribution but also to maintain this distribution as the dendrite is withdrawn from the melt.

Operation of the above-described apparatus and an example of the method of growing α -alumina filaments according to my invention will now be described. An α -alumina seed crystal 38 is mounted in holder 36 with its C-axis aligned parallel to the holder's path of movement. At the same time a quantity of substantially pure α -alumina is placed in crucible 46, orifice plate 52 is placed on top of the alumina, and then the crucible is placed within susceptor 40 on tungsten rod 44. Access to the seed holder and the susceptor is achieved by lowering bed 2 away from the furnace enclosure and lowering the seed holder to below the bottom end of tube 4. With the bed restored to the position of FIG. 1, cooling water is introduced between the walls of the two quartz tubes, and the enclosure is evacuated and then filled with helium. The latter is kept at a pressure of about 1 atmosphere thereafter. Then the R.F. coil is energized and operated so that the α -alumina is brought to a molten condition. It is to be noted that the orifice plate does not sink into the melt but floats at its surface, even though the plate's density is greater than that of the melt. The reason for this is that the melt does not wet molybdenum. The α -alumina is brought to a temperature slightly above its melting point which is in the range of 2040 to 2050° C. In this molten condition the height of the meniscus 56 of the alumina in orifice 54 is an inverse function of the diameter of the orifice and typically is almost flush with the top surface of the orifice plate. Once tempera-

ture equilibrium is established, the pulling mechanism is actuated and operated so as to bring the seed crystal 38 into contact with the meniscus. Almost immediately thereafter the pulling mechanism is operated so as to pull the crystal at a predetermined rate of speed. The melt temperature is critical and in the usual case initial withdrawal of the seed is unaccompanied by continuous growth. At this point it is to be appreciated that if the surface of the melt is too cold, nothing will happen when the seed touches the meniscus; on the other hand, if the surface of the melt is too hot, the seed will melt. The temperature of the melt is adjusted accordingly and the seed again is brought into contact with the melt. At the proper melt temperature, dendritic growth will occur on the end of the seed. Thereafter the seed is withdrawn at a speed corresponding to the rate at which the dendrite growth propagates down into the melt. If the seed continues to be withdrawn at the proper speed, the growth will be continuous until the melt is depleted. The orifice plate will settle within the crucible as the alumina is depleted. The maximum length has been limited only by the maximum pulling distance afforded by pulling mechanism 34.

The habit of the filament-like crystals produced according to the foregoing method has shown variations that can be generalized into four different types, all of which have been grown using a sapphire seed crystal oriented with its C-axis parallel to the axis of the seed holder. One habit is characterized by a rather uniform outer surface and a circular cross-section. The other habits all have more or less rectangular cross-sections, but the outer surface of one has irregular undulations, another is stepped longitudinally, and the third appears to be twisted longitudinally. All of these different habits have easily discernible features. Although the filaments appear to be single crystals, some samples show evidence of a twin morphology. Thus those filaments that appear to be twisted longitudinally may in fact be twinned since the crystal ends often are characterized by two discrete points. In this connection reference is had to Dana, "System of Mineralogy," 7 ed., p. 522, John Wiley & Sons, Inc., 1963, which discloses that α -alumina (also known as corundum) belongs to the hexagonal group and forms a lamella structure in the (10 $\bar{1}$ 1) plane and also a less common twin on (0001). An additional feature is that it is subject to pressure twinning, i.e., twinning can be caused in a seed crystal by application of appropriate shear pressure.

After a particular habit has been nucleated and propagated, it is possible to separate the grown filament from the melt by fast retraction, reinsert it into the melt and then resume normal growth procedure. The dendrite filament that grows afterward will be the same crystal type as that originally propagated before separation from the melt. Laue X-ray back reflection photographs of some sample filaments reveal certain interesting facts. One Laue back reflection photograph of a filament grown on a C-axis oriented sapphire seed revealed three-fold symmetry except that each reflection was split into three or four spots. This suggests the presence of three or four crystals with their C-axis approximately parallel to the filament axis but slightly misoriented with respect to each other. Other filaments give still more complex patterns but generally still with the features of three-fold symmetry. By contrast a Laue back reflection of a sapphire filament grown onto a tungsten seed did not display any apparent three-fold symmetry along the filament axis.

A further interesting phenomenon is that the cross-sectional shape and sizes of the filaments do not conform to the shape and size of the orifice through which they are pulled. This is different from what occurs in other crystal growing processes where a melt is extruded through a die. Thus, for example, in the process disclosed in U.S. Pat. No. 3,124,489, issued Mar. 10, 1964, to F. F. Vogel, Jr. et al., for "Method of Continuously Growing Thin Strip Crystals," the germanium ribbon pulled from the melt through a carbon die has a cross-section

of the same shape and substantially the same area as the die passage exit. The difference is attributable to the fact that in my process the crystal grows dendritically down into the melt, i.e., the solid/liquid interface of the filament is below the melt surface, while in the process of Vogel et al., the molten material solidifies within or above the die passage. The orifice plate used in my process does not shape the filament, except insofar as the plate shapes the temperature gradients. The filament shape appears to be affected by the temperature gradients, the average temperature of the melt, and the orientation of the seed crystal. The rate of pull appears to affect the size of the filament and to some extent its shape.

In this connection it appears from observation that the molybdenum orifice plate has a lower total emissivity than alumina at temperatures in the order of 2000° C. Accordingly it is believed that this property enables the floating plate to act as a heat shield which limits the heat loss from the melt surface and thereby controls the radial and longitudinal temperature gradients in the immediate vicinity of the small surface of the melt exposed within the orifice. The heat shielding effect of the floating plate not only establishes the correct temperature distribution required to promote propagation vertically but also permits the melt to be supercooled in the region where the seed is introduced, an essential condition for dendritic growth. In summary the floating molybdenum plate serves the dual function of providing an effective heat shield and an exposed central growth orifice of any chosen diameter.

A definite indication of the fact that growth is dendritic is the speed at which the filament may be pulled from the melt. In practice I have pulled filaments at speeds up to about 150 mm./min. using a floating plate with an orifice having a diameter of $\frac{1}{32}$ inch. This is substantially in excess of the one inch/min. speed employed in growing germanium strip crystal using the process of Vogel et al., cited above. It is believed that growth rates substantially faster than 150 mm./min. can be achieved if the heat loss from the filament (primarily radiative in the apparatus and process described above) is augmented by forced convection. It also is to be appreciated that with proper control, simultaneous growth of a plurality of filaments from a common melt may be achieved using an orifice plate with a number of orifices located so that each meniscus is at approximately the same temperature.

Although I prefer to mount the seed crystal so that growth occurs along its C-axis $\langle 0001 \rangle$, it may also be mounted so that its C-axis is at an angle to the axis of the crystal holder. Moreover a twinned seed may be used. It also is to be understood that the process need not be carried out in a helium or argon atmosphere; instead the furnace enclosure may be evacuated to a suitable level.

In addition to the fact that it permits growth of alumina in filament form, the invention has several other advantages. For one thing the apparatus for producing the thermal conditions essential to dendritic growth is simple and the floating orifice plate is not restricted to use with the particular furnace design illustrated in the drawings but may be employed in other apparatus adapted to pull crystals from a melt. Another advantage is that the process may be used to grow ruby filaments. Perhaps the most important advantage is that it provides a new and useful form of α -alumina, i.e., extended filaments. In this connection it is to be noted that I have grown sapphire filaments measuring 6 inches in length and 0.13 to 0.50 mm. in diameter at pulling rates up to 150 mm./min. It is to be appreciated that the length of these filaments was not limited by the process per se but only by the capability of pulling mechanism 34, and production of filaments with lengths in the order of tens of feet and higher is contingent only upon provision of apparatus of greater pulling capacity. Sample sapphire filaments produced in the manner described above have been found to have an elastic modulus of $30\text{--}50 \times 10^6$

p.s.i. (as measured by the vibrating Reed technique), a flexure modulus of 25×10^6 p.s.i., and a tensile strength of at least 125,000 p.s.i.

As used herein the term "filament" is not limited to a crystalline product of circular cross-section but also embraces polygonal cross-sections.

It is to be understood that the invention is not limited in its application to the details of construction and arrangement of parts specifically described or illustrated, and that within the scope of the appended claims, it may be practiced otherwise than as specifically described or illustrated.

I claim:

1. Apparatus for producing a filament of crystalline alpha-alumina comprising a furnace enclosure, a crucible in said enclosure adapted to contain a supply of alumina, means for heating said crucible to melt said alumina and hold it at a selected temperature above its melting point, said crucible including a plate with an orifice that is adapted to float on the surface of said melt and to reduce radiative heat loss from said melt so as to produce in said melt a thermal distribution conducive to crystal growth propagated vertically in a region of said melt exposed by said orifice, said crucible and plate being made of molybdenum or iridium, and means for positioning a seed crystal in said orifice so that crystal growth can occur thereon and for withdrawing said seed with its grown crystal at a rate consistent with the rate of crystal growth propagated.

2. Apparatus as defined by claim 1 wherein said crucible is made of molybdenum.

3. Apparatus as defined by claim 2 wherein said plate is made of molybdenum.

4. Apparatus as defined by claim 1 wherein said crucible is made of iridium.

5. Apparatus as defined by claim 1 wherein said plate is made of iridium.

6. A method of producing a filament of crystalline alpha-alumina comprising providing in a crucible made of molybdenum or iridium a melt of alumina and a plate floating in said melt at the surface thereof, said plate having an aperture and being made of molybdenum or iridium, adjusting the temperature of said melt so that

crystal growth propagating vertically will occur on a seed introduced into a region of said melt exposed by said aperture inserting a seed crystal into said region by way of said aperture for a period of time sufficient for crystal growth to occur thereon, and pulling said seed upwardly away from said melt at a speed not exceeding the rate at which said crystal growth propagates vertically so that successive accretions of grown crystal form an extended filament.

7. Method of claim 6 wherein said crucible is made of molybdenum.

8. Method of claim 7 wherein said plate is made of molybdenum.

9. Method of claim 6 wherein said crucible is made of iridium.

10. Method of claim 6 wherein said plate made of iridium.

11. Method of claim 6 wherein said seed is withdrawn at a speed in the order of 150 mm./min.

12. Method of claim 6 wherein said seed is a single crystal having a C-axis and is oriented so that said C-axis extends substantially vertically.

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